* + 1. ***Alkalinity*** 
       1. ***Sampling***

During the 2013-05 cruise, seawater samples were collected for DIC/alkalinity analysis from the surface and bottom depth (max = 122 m) at 25 stations into 250 ml glass bottles. At 2 selected stations, full depth profiles were collected. Since all samples from this cruise were analyzed post-cruise, 100 μL of saturated mercuric chloride solution was added and glass stoppers greased to seal the sample bottles for preservation.

A total 73 samples were collected from Niskin bottles. Of these, 1 sample was taken in duplicate.

#### Analysis

Samples were analyzed for DIC first, and then seawater left in the bottle was analyzed for alkalinity onshore, at DFO-IOS, by Marty Davelaar in January-February 2014. Samples were put in water bath (25°C) at least 20 minutes before being analyzed. The total alkalinity was determined by potentiometric titration using 0.1N HCl/0.6N NaCl, using a program written by Paul Covert, PMEL, University of Washington which is based on Andrew Dickson’s, SCRIPPS, system. Alkalinity values are reported in units of µmol/kg.

At the start of each day, seawater was run through the system to condition the instruments. Once the system appeared to be working well, certified reference material (CRM) was run to confirm proper operation. The concentration of acid was calculated to give the assigned alkalinity values for CRM. For both CRM and sample analysis approximately 100 grams of 25°C seawater is poured into a beaker. The exact weight of the liquid is then entered into the program before the titration is started.

An initial amount (ranged from 1.6 to 1.8 mL) of the HCl/NaCl was added to the seawater and then 0.04 mL aliquots of acid were added to the seawater until a pH of below 3.55 was obtained. The sample was then stirred for 360 seconds to degas CO2, the reading of pH (EMF) and addition of 0.04 mL of acid were repeated until a final pH of below 2.995 was reached.

A plot of total alkalinity measurements versus CTD-salinity or CTD-depth was made simultaneously during analysis, and samples that seemed unusual in the plot were re-analyzed. Drift throughout the day was monitored by checking the values of CRM samples.

#### Precision and Standards

Table . Water Sample Precision

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Chemistry Sample** | **Precision (%CV)** | **Accuracy (%recovery)** | **Units** | **Number of Replicates (n)** | **Outliers removed** | **Minimum Range** | **Maximum Range** |
| DIC | 0.14 | 99.87 | µmol/kg | 9 | 0 | 1937.12 | 2307.43 |

The accuracy of the alkalinity analysis was assured by daily analysis of certified reference material (batch 123, salinity = 33.341 psu, alkalinity=2224.37 µmol/kg; DOE 1994; Dickson 2001; Dickson et al. 2003) supplied by Andrew Dickson (Scripps Institute of Oceanography, San Diego, USA). The accuracy (%recovery = measured CRM / certified CRM X 100) was on average 99.87%, and varied from 99.76 to 100.13%.

Precision was calculated as the percent coefficient variation (%CV = standard deviation of the mean CRM / mean of the CRM X 100) as only 1 duplicate was collected and so the pooled standard deviation could not be computed. The %CV was excellent, at 0.14% for the 9 days of analysis.